



Research paper

One-step hydrothermal synthesis of Bi-TiO₂ nanotube/graphene composites: An efficient photocatalyst for spectacular degradation of organic pollutants under visible light irradiation

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ABSTRACT

In the present study, we have adopted a simple one-pot alkaline hydrothermal route to synthesize Bi-doped TiO₂NT/graphene composites by using different wt% of Bi with an aim to achieve the excellent photocatalytic activity under visible light source. The nature of GO is changed to deoxygenated graphene with simultaneous embedding of Bi into TiO₂ nanotube (TNT), during hydrothermal process. XRD and FTIR analysis confirm the successful conversion of GO to deoxygenated graphene. EPR analysis reveals the co-existence of Ti³⁺ ion with oxygen vacancy, which is created by the Bi doping. The photocatalytic activity of the prepared samples is measured by the degradation of aqueous suspensions of methylene blue (MB) and Dinoseb (phenolic herbicide), under visible-light irradiation. The prepared TiO₂NT/graphene composite with 2-wt% bismuth (2-BTNTG) has shown the improved photocatalytic activity as compared to their counterparts. The improved photocatalytic activity is associated to the synergistic effect of graphene and Bi-TNT, which facilitate the interfacial charge transfer and enhances the efficiency of light harvesting in the visible region. Moreover, the underlying mechanism involving photocatalytic degradation of organic pollutants over 2-BTNTG is explored by using trapping experiments, suggesting that the ·OH radicals solely contributed to degradation.

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1. Introduction

Recently, a wide variety of organic pollutants comprising of herbicide derivatives, textile dyes, and phenolic compound derivatives responsible for environmental and water pollution are reported [1–3]. Among these, herbicide derivatives and textiles dyes are most difficult to decompose owing to their chemical and biological stability [4–7]. These are ranked as the most carcinogenic and high toxic pollutants, manifesting the major threat to human and aquatic life [8–10]. Enormous research efforts are devoted to reduce these pollutants in water by biological and physical techniques but the majority of these are cumbersome, expensive and less effective [11–13]. In this regard, semiconductor photocatalysis is emerging as an advanced and green technology for the degradation

of these pollutants due to its environmental benignancy, stability, and safety [14,15]. Significantly, TiO₂ has proven to be one of the most widely accepted and benchmark photocatalytic material owing to its strong oxidizing power, intoxicate high photostability, and low cost [16–19]. One-dimensional (1D) nanostructures of TiO₂, such as nanorods [20], nanowires [21], and nanotubes [22,23], have gained interest owing to their quantum confinement and high surface area. TiO₂ nanotubes are widely applied in the photocatalytic degradation of organic pollutants because of their structure dependent enhanced photocatalytic properties [23–25]. However, the major drawbacks that confine its use to larger scale are its wide bandgap and quick recombination of charge carriers [25–27]. Several strategies are adopted to modify TiO₂ such as extending its spectral response to the visible region and prolonging the life span of photoinduced electron-hole pairs. The strategies involve, doping with metals and non-metals [27–29], noble metals deposition [30] and heterostructure construction with narrow bandgap semiconductors and carbonaceous materials [31–35]. The carbon-titania nanocomposites by linking titania with carbonaceous materials

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have received much attention as a new class of photocatalysts, which could boost its photocatalytic activity by separating charge carriers and electron transfer from TiO₂ to carbonaceous materials on irradiation [33–38].

Graphene is also used as most suitable two-dimensional nanosheet photocatalyst in the arena of photocatalysis owing to its high surface and superior electron mobility [39–41]. The excited electrons from the semiconductor materials are effectively trapped by the graphene, which hinders the recombination process ultimately enhancing the photocatalytic activity [35,36,38]. In literature, the intimate contact between graphene and TiO₂ has immensely improved the photocatalytic activity because of their π -conjugation system and 2D planar structure. This tends dye molecules to adsorb on their surface more easily through π - π stacking between aromatic regions of graphene and dye molecules [42,43].

Nevertheless, some problem still restrains further promotion of efficiency of the present graphene-based TiO₂ nanocomposites, i.e. weakening of light harvesting efficacy of catalyst which results in the generation of the small fraction of charge carriers, consequently impairing the photocatalytic activity. In order to make full use of solar energy and further alleviate the recombination rate of charge carriers, metal ions doping is found as the most effective way to satiate the above conditions and thus promote the photocatalytic reactions. For instance, Nguyen-phan group has developed a hydrothermal method to synthesize Sn-doped TiO₂ nanoparticles supported onto reduced graphene oxide (rGO) with superior photocatalytic activity [44]. Qian and his co-workers have reported the synthesis of N-doped TiO₂/graphene composites with prolonged electron life time for high-performance photocatalytic degradation due to the synergetic action of graphene and N-doped TiO₂ [45]. Chen et al. have reported the synthesis of Mn-doped TiO₂ grown on graphene via one-pot hydrothermal method, which showed the highest photocatalytic activity for the removal of Cr(VI) and Cr(III) under sunlight [46]. These researches reveal that the simultaneous incorporation of graphene and metal ions can significantly improve the photocatalytic activity of semiconducting materials to the larger extent.

In recent years most of the researches are inclined to the formation of bismuth-doped TiO₂ nanostructures via hydrothermal method, which can improve the photocatalytic activity for the removal of organic pollutants owing to its ability to take advantage of the broad range of solar spectrum [47–50]. Bismuth-doped TiO₂ nanofibers are prepared by an alkaline hydrothermal approach that showed the structure dependent enhanced photocatalytic activity for hydrogen production as well as MO degradation under both UV and visible light irradiation [51]. A literature reported on the synthesis of bismuth doped TiO₂ hollow thin sheet with enhanced photocatalytic activity towards the decomposition of different kinds of organic pollutants [27]. Considering the respective advantages of graphene and Bi doping, it could be speculated that combined effects would be effective to attain the highest photocatalytic activity under visible light illumination. However, to the best of our knowledge, it has not yet been reported in the literature, i.e. the combined effect of graphene and Bi for the photocatalytic decomposition of MB and herbicide derivative.

In the present work, combining the doping effect, nanostructures and graphene, we design an efficient photocatalyst comprising Bi-TiO₂ nanotube grown on reduced graphene oxide sheets through a facile alkaline hydrothermal approach. The notable aspect of our approach is the simultaneous reduction of GO to graphene and incorporation of Bi into TiO₂NT. The prepared composites are characterized and their photocatalytic activities are evaluated by studying the decomposition of organic pollutants (Dinoseb and MB) under visible light irradiation.

2. Experimental details

2.1. Reagents and chemicals

All the chemicals were of analytical grade and were used without further purification. Bismuth nitrate [Bi(NO₃)₃·5H₂O] was purchased from central drug house (CDH) and commercially available TiO₂ nanoparticles (Degussa P25) was a gift sample from Evonik-Degussa, Germany. The model pollutants such as Dinoseb and methylene blue (MB) used for the degradation studies were obtained from Sigma-Aldrich. The other reagent grade chemicals used in this study, such as sodium hydroxide, sulphuric acid, sodium nitrate, potassium permanganate, hydrogen chloride, terephthalic acid (TA), isopropyl alcohol (IPA), benzoquinone, and ethylenediaminetetraacetate (EDTA-2 Na) were obtained from Merck.

2.2. Preparation of samples

A series of bismuth doped TiO₂ nanotube graphene (Bi-TNTG) composites with different contents of bismuth (1–4 wt% with respect to Ti) were prepared by a facile alkaline hydrothermal approach initially developed by Kagusa [52]. Graphene oxide (GO) was synthesized from commercially available graphite powder using a modified Hummer's method [53]. A flow chart showing the method involved in the preparation of Bi-doped TiO₂ NT/graphene composites is illustrated in Scheme 1. In a typical process, desired amount (2 wt%) of synthesized GO was suspended into 30 mL of double distilled water and sonicated for 90 min to which 1 g of Degussa P25 was added. A separately dissolved various amount of bismuth nitrate in water was added into above solution and stirred for 1 h to obtain a homogenous suspension. In order to make the above solution concentration up to 10 M, required amount of NaOH was added with vigorous stirring. After 1 h of stirring, the complete mixture was transferred into a Teflon-lined autoclave and heated at 140 °C for 24 h and then cooled down to room temperature. The final grayish color product was filtered and washed with double distilled water followed by acid washing with 0.1 M of HCl, which was then dried at 80 °C for 16 h. Subsequently, the obtained product was rinsed multiple times with double distilled water and then the product was allowed to dry overnight at 80 °C and then ground to obtain a fine powder. It was further subjected to annealing process at 350 °C for 6 h. The final Bi-doped TiO₂ NT/graphene composites were denoted as x-BTNTG, where x stands for 0, 1, 2, 3, 4 wt% of Bi. Single Bi-doped TiO₂ NT and bare TiO₂ NT were also prepared by the similar procedure, but not including the amount of Bi and/or GO.

2.3. Materials characterization

X-ray powder diffraction patterns of prepared samples were obtained using Shimadzu XRD (model 6100) with (Cu K α radiation (1.54065 Å)) operated at a voltage of 30 kV and current of 15 mA. Fourier Transform Infrared spectra were acquired in the range of 400–4000 cm⁻¹ using a Perkin Elmer spectrum-2. Scanning electron microscopy and energy dispersive spectra were obtained using JEOL-JEM with an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images of the catalyst were obtained by using a JEOL-JEM 2100 microscope at an accelerating voltage of 120 kV. The optical properties of the samples were determined by UV-vis diffuse reflectance spectra (DRS) using Perkin Elmer Lambda 35 UV-vis spectrophotometer. The spectra were acquired at 300–800 nm using BaSO₄ as a reflectance reference. Electron paramagnetic resonance (EPR) spectra were recorded at 100 K using JEOL-JES-FA200 ESR spectrometer. Brunauer Emmett-Teller specific surface areas (S_{BET}) of the photocatalysts were determined

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